1,143,502

PATENT SPECIFICATION

NO DRAWINGS

1,143,502

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COMPLETE SPECIFICATION

Improvements relating to Synthetic Resin Dough Compositions, a Dental Package including such Compositions and to Artificial Teeth made from such Compositions

We, WILLIAMS GOLD REFINING CO. INCORPORATED, a corporation of the State of New York, of 2978 Main Street, Buffalo, New York, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel, pasty, polymerizable synthetic resin dough composition useful in cured form as a hard, tough, dental product and especially useful in the form of a composite artificial plastic tooth, and also useful as a dental patching, restoring or sealing composition in the form of a preformed strip of putty, generally pigmented to match a natural tooth. The pasty dough composition of the invention is uniquetly characterized by its very low volatility and its long shelf life at room temperature (at least six months and longer) before curing and by its outstanding wear-resistance and toughness after curing. Both of these advantageous attributes are unexpectedly superior in dental dough as compared with the standard methacrylate dough mixture of the prior art.

According to the present invention, a pasty, polymerizable synthetic resin dough composition consists of a polymerizable mixture of a solid finely divided methyl methacrylate polymer, and a polmerizable liquid dimethacrylate or diacrylate ester, said ester being the sole liquid component of the composition and being derived from a polyhydric aliphatic alcohol containing from 3 to 8 carbon atoms, or a polyethylene glycol having a degree of polymerization from 2 to 6, or a polypropylene glycol having a degree of polymerization from 2 to 6, said ester being less volatile than dibutyl phthalate.

Since both the solid phase and the liquid phase of dough putty consist of an optically transparent material, there results from polymerization of the putty a mixed resin having highly desirable transparency qualities which provide the advanage of accurate and faithful colour and shade reproducibility when matching pigmented dough formulations to natural teeth. The liquid non-volatile dimethacrylate or diacrylate ester, which is the sole material constituting the liquid phase in which the resin filler and pigment may be dispersed, has excellent wetting properties for opacifying inert, stable, solid pigments which are acceptable for dental use, e.g., such pigments as titnaium dioxide, zinc oxide, copper oxide, iron oxide, cobalt oxide, barium sulphate, carbon black, burnt umber, cadmium selenide, cadmium sulphide and mixtures of the foregoing.

The present invention is based upon the discovery that, while certain non-volatile monomers are very well suited for use in the manufacture of artificial composite teeth, they are too brittle for use as repairing, restoring and patching material. It would be expected that dimethacrylate or diacrylate esters would be so brittle as to be totally unsuitable for use as a tooth. A sharp blow made to an outer surface of the brittle dimethacrylate or diacrylate ester would shatter it. Indeed, it is unexpected to find that the tooth structure will resist shattering if made in composite form by moulding an outer portion consisting of the present dough composition about and around a central core portion consisting of solid polymethyl methacrylate.

A composite tooth structure consisting of a polymethyl methacrylate core and a wear-resistant outer plastic material is known and methods for manufacturing such a tooth

are known. An example of a composite tooth structure is described in the U.S. patent to Gotlib, No. 2,793,436, or to Saffir, No. 2,477,268. Methods for manufacturing composite teeth are described in Feagin, U.S. patent No. 2,528,219. The advantages obtained depend on the composition of the outer plastic material, a first possible composition being based upon non-volatile, somewhat brittle materials and a second possible composition embracing all but the butylene and propylene glycols in the first group.

Heretofore, it was thought that none of these polyglycols could be made in non-porous embodiments without being unduly brittle. Indeed, the only known use for the pure solid diester is the highly porous, prosthetic product of Wichterle et al. in U.S. patent No. 2,976,576, granted March 28, 1961. It was proposed by Wichterle et al. to use the product as a sponge, filter or surgical implant in blood vessels. It is important to note that Wichterle et al. polymerize the monomer alone and did not attempt any processing of the dough mixtures.

The liquid component of the mixture used for preparing a tooth consists of a dimethacrylate ester of a polyhydric aliphatic alcohol having from 3 to 8 carbon atoms or a polyethylene glycol having a degree of polymerization of 2 to 6 or polypropylene glycol having a degree of polymerization of 2 to 6, while in the patching, restoring or sealing material, hereinafter called veneer gel, the dimethacrylate or diacrylate ester is preferably derived from a polyhydric aliphatic alcohol having from 5 to 8 carbon atoms, or a polyethylene glycol having a degree of polymerisation of 2 to 6, or a polypropylene glycol having a degree of polymerization of 2 to 6.

The distinction between these two types is based also upon the volatility characteristics.

The non-volatile difunctional monomers which are unsuitable for use as veneer gels, although suitable for the manufacture of composite acrylic teeth, are butylene glycol dimethacrylates and diacrylates in which both linear and branched types of butylene glycol are present and the propylene glycol dimethacrylates and diacrylates which are both of the linear and branched types.

Dibutyl phthalate is one of the standard materials of non-volatile characteristics, acknowledged in the art as a non-volatile material which is compared to the non-volatile liquid component of the present invention.

Another component which is compared is methyl methacrylate monomer having a boiling point of 100°C.

A third component is ethylene glycol dimethacrylate, hereinafter called EDMA. This material is the standard cross-linking agent in commerce and is excluded in the veneer gel of the present invention.

The following illustrates the characteristics of non-volatility which resulted in excluding EDMA and including triethylene glycol dimethacrylate.

The volatility of monomeric triethylene glycol dimethacrylate, the preferred cross-linking monomer phase, is only very slight. The following vapour pressure and temperature data are submitted in order to compare the cross-linker constituting the entire monomer phase of the dental dough with methyl methacrylate and dibutyl phthalate.

VAPOUR PRESSURE in mm. Hg

	0°C.	*50°C.*	*100°C.*	*150°C.*
Methyl methacrylate	8.5	125	760	
Dibutyl phthalate	0.001	0.008	0.1	1.5
Triethylene glycol dimethacrylate (TEDMA)	0.001	0.01	0.01	1
Tetraethylene glycol dimethacrylate	0.001	0.01	0.01	0.1
Polyethylene glycol 200 dimethacrylate	0.01	0.01	0.01	2
1,3-Butylene glycol dimethacrylate	0.01	0.1	1	15
Ethylene glycol dimethacrylate (EDMA)	0.01	0.1	8	120

The volatility of EDMA at 100°C. is such that about 4% evaporates in 4 hours at 100°C. and about 8% evaporates in 8 hours.

The solvating power of EDMA at 100°C. is very much greater than that of TEDMA at 100°C. Similarly, the solvating power of ethylene glycol dimethacrylate is so great that at room temperature a mixture of polymer and monomer, using ethylene glycol dimethacrylate, will gel and become too stiff to be operable.

Given the same reaction conditions, the cross-linking density of EDMA is so high that cured EDMA dough products are excessively brittle while TEDMA products are not objectionably brittle due to the longer chain, more flexible, structure. Also, each of the dimethacrylates, including the more

volatile EDMA, provides compositions which are completely impervious to water and are also resistant to saponification by chemical agents present in the mouth. It is believed that, as a result of these characterisics which are inherent in the chain structure as well as in the ester portion of the molecule, there is provided a beneficial plasticizing action to the cured tooth decreasing brittleness which is completely surprising in view of its effectiveness as a cross-linking agent.

These characteristics are to be contrasted with glycol diacetate and diglycol diacetate. An illustration is given in terms of glycol diacetate which is an excellent solvent and dissolves much more polymer than dibutyl phthalate to form a stickier dough which is more difficult to mix. At the processing temperature of 100°C. glycol diacetate has a very high evaporation rate. In about 4 hours 30% will evaporate, during a 9 hour shift 40% will evaporate, and in 16 hours 60% will evaporate. Thus, if this plasticizer is incorporated into a denture and heated to 100°C. overnight, the majority of this liquid softening agent will be lost by such heating. It is also extractable from the completed denture imparting no permanence to the flexibility obtained, and quite different from the hardness and toughness imparted by the higher glycol dimethacrylates.

Using diethylene glycol diacetate as a replacement overcomes the problem of volatility but does not overcome the problem of stiffer dough, since the diacetate is also a very strong solvent for methyl methacrylate polymer, e.g., stronger than dibutyl phthalate, and processing by mixing and shaping is much more difficult. More serious, however, is the drawback that liquid glycol diacetate or diglycol diacetate is soluble in water, e.g., 14.3 grams of glycol diacetate dissolved in 100 millilitres of water at room temperature and the solubility of the diglycol diacetate is above 6-8% and is extracted in the mouth.

Glycol diacetate is about 100 times less volatile at room temperature than methyl methacrylate. Using the test mehod of Doolittle in "Industrial Eng. Chem., Vol. 27, p. 1169 (1935)" glycol diacetate provides an evaporation rate figure of 100% evaporated after 375 hours at room temperature (25°C.) and atmospheric pressure. Under these conditions methyl methacrylate evaporates 100% in 2.1 hours and diglycol diacetate evaporates 2% in 500 hours.

At elevated temperatures of 100°C. at which the dental dough composition is cured, the vapor pressure of the standard plasticizer is sufficiently high that it must be taken into account during manufacturing in order to achieve a high quality cured dental dough.

This volatility effect is complicated by the enhanced solvency effects which cause more polymer to be dissolved in the monomer over an extended time period thus in turn increasing the viscosity and reducing the workability of the dough. There follows a corrected table of vapour pressures at different temperatures taking account of these effects.

VAPOUR PRESSURE IN mm. Hg AT DIFFERENT TEMPERATURES °C.

Ester	*0.1 mm*	*1 mm*	*5 mm*	*10mm*	*760 mm*
Dibutyl phthalate	113°	148°	180°	195°	340°C.
Dibenzyl phthalate	185	250	—	—	277 (with decomposition)
Tricresyl phosphate	155	200	234	250	—
*TEDMA (SR 205)	115	150	168	185	—
2-Methyl,3-glycol phthalate	129	163	202	218	—
Polyglycol dimethacrylate	105	145	160	—	—
**EDMA (SR 206)	—	—	95	114	350
Butylene glycol dimethacrylate	73	103	128	140	290

*TEDMA=triethylene glycol dimethacrylate
**EDMA =ethylene glycol dimethacrylate

The veneer gel restorative products of the invention are outstanding because of their relatively high density and absolute freedom of porosity, a result which is not expected in view of the teaching of Wichterle et al. U.S. 2,976,576. Especially unexpected are the outstanding properties found in the invention of wear resistance, hardness, toughness without brittleness, ageing resistance and impact resistance in view of the brittleness of highly strained bulk polymerized solid dimethacrylate, such as EDMA, which was to be expected.

The standard dental gel polymer in den-

sity is based on methyl methacrylate polymer and methyl methacrylate monomer dough mixed in proportions of 20-40% of monomer and 80-60% of polymer by weight, as disclosed in Vernon et al. U.S. Patent No. 2,234,993, this mixture being tinted, pigmented or shaded. The dough is polymerized by moulding at elevated temperatures of up to about 105°C. in the dental flask and at pressures of up to 700 pounds per square inch to simulate the desired part of teeth, palate or gum tissue. About 5-15% by weight dibutyl phthalate plasticizer is used to improve the moisture resistance of the polymer. The polymer which has been plasticized with dibutyl phthalate shows improved moulding and handling characteristics.

Due to the reactivity of polymerization of methyl methacrylate monomer in the presence of residual catalyst at room temperature, this Vernon et al type of dough mixture has to be stored at low temperatures, e.g., in a refrigerator, and in a hermetically sealed container in order to prevent the slow hardening by evaporation of the monomer due to high vapour pressure of the monomer at room temperature (see Vernon U.S. Patent No. 2,234,993, page 2, column 1, line 74 to column 2, line 2). Once hardened on storage, the Vernon type dough gel cannot be handled at all, and even when stored under the most favourable conditions, it is difficult to handle, e.g., it cannot easily be cut or shaped in the dental mould even though it has been plasticized with dibutyl phthalate. If excess momomer is added to soften, excessive shrinkage occurs on moulding.

Efforts have been made by others to improve this gel, as for example, by Crowell et al. in U.S. Patent No. 2,315,503 and by Gordon in U.S. Patent No. 2,874,832. Crowell et al. proposed that a vinyl ester polymer be used for the solid phase but the kind and amount of reactive monomer, e.g., methyl methacrylate in proportions of 10-40 weight per cent based on the total weight of the mixture has rendered the vinyl gel subject to the same defects of high viscosity, poor storability and limited shelf life as the Vernon type gel.

Fox and Loshaek reported efforts to improve the gel in the Journal of Polymer Science, 1951, and suggested that ethylene glycol dimethacrylate, propylene glycol dimethacrylate and hexamethylene glycol dimethacrylate be used to cross-link in mixture with methyl methacrylate monomer in copolymerization in bulk but they found cross-linking efficiencies of between 60-80% in the presence of a free radical polymerization catalyst and temperature of about 80°C., the copolymerization method being a commercially practical bulk system. Increasing proportions of methyl methacrylate monomer were considered by Fox et al. to be essential and the monofunctional monomer was increased in order to promote the efficiency of polymerization of cross-linking agent whereby the per cent of cross-linked groups in the polymer relative to those available was increased, although the total number of cross-links fell. On the basis of this pioneer work, it was expected by those conversant in the art that as the proportion of ethylene glycol dimethacrylate increases from 10 to 20% by weight in the ethylene glycol dimethacrylate-methyl methacrylate liquid system, the peroxide cured products made at 80°C. become increasingly harder, increasingly brittle and increasingly strained. This last characteristic of increasing internal strain means that the mould product in the form of a strip cannot be subjected to grinding or cutting with a sharp tool without fracturing or being liable to fracture along cleavage lines and along internal strain patterns to produce chunks of glossy plastic.

Accordingly, the amounts of cross-linking agents of the ethylene glycol dimethacrylate type have been limited to a predetermined maximum which, if exceeded, is liable to cause excessive internal strains. This amount is recognised as being dependent on temperature of curing, rate of cure, efficiency of cure and accommodation through annealing. Since the peroxide initiator is generally a standard amount and the temperature is controlled within narrow predetermined limits in the dental flask method, there is no alternative before the present invention in dealing with the strain problem except the cutting down of the degree of cross-linking to prevent strain and to look for a limit of cross-linking to achieve the desired hardening benefit.

Increasing lengths of the chain between alkyl groups in the cross linker provides a low molar cross-linking on a weight basis and a relatively higher efficiency so that sufficient conversion to cross-linked polymer increases the benefits of cross-linking with a loss of hardness. Fo rthis reason and based on cost, the practice heretofore was based on ethylene glycol dimethacrylate with the upper limit held below about 25 mol per cent even though this cross-linker was less efficient on a weight basis than the longer chain cross-linkers.

Accordingly, prior to the present invention it was not expected that one could achieve formable plastic products free from shattering on grinding and cutting by utilizing cross-linking agents as the only component of the monomer phase. This defective inherent characteristic of ethylene glycol dimethacrylate is also exhibited by trimethylol propane trimethacrylate, but the latter is

worse in imparting strain when bulk polymerized with benzoyl peroxide, or bulk copolymerized with a small amount of methyl methacrylate. It is not readily useful for moulding in the presence of other polymer or as the unmodified product, and this defect has made the monomer non-commercial in the use as a homopolymer.

In every instance of homopolymer there are produced brittle products from the diacrylates which have such an inherent tendency to shatter that they cannot be used for whole teeth or for tooth patching material having waterproofing properties.

If these trimethylol propane trimethacrylate products were especially plasticized and properly polymerized by special techniques to provide complex blends, the shattering defect might be overcome but the result could be hardly worth while or suitable for general dental use. In this area of application, the requirement for resistance to mechanical extraction, ageing resistance, resistance to moisture, resistance to abrasion and impact, and colour stability are so difficult to achieve with plasticized mixtures of this type, that the effort for veneer gel use cannot be expected to succeed.

It was, therefore, wholly unexpected and surprising that the present cross-linkers constituting the entire monomer phase be superior in wear resistance to the conventional cross-linked methyl methacrylate veneer gel or cross-linked methyl methacrylate tooth.

Ethylene glycol dimethacrylate as monomer in the dough system is further unsuitable because solvating power is unduly high and yields a stiff gel which becomes very hard and quickly unworkable, either due to extraction of the catalyst from the polymer or due to simple solvation of the polymer by the monomer to give extremely high viscosity.

Trimethylol propane trimethacrylate is at the other extreme as far as solvency is concerned and is a very poor solvent in the dough system. With the dental polymer in an amount used in a preferred composition, no solvation is observed at room temperature and the composition remains sandy so as to be completely unsuitable for moulding and forming in the dental flask. If the composition is moulded after special premixing, the tooth obtained is so excessively brittle as to be completely useless.

The polymer in the dough can be prepared in which there is no residual peroxide and this can be used to improve the dough. For example, it is possible to heat the polymer for 16 hours such that an analysis for residual peroxide shows none. This polymer when mixed with the preferred monomer concentration will not cure in 30 minutes at 212°F., or in 60 minutes, so that it is seen, as a practical matter, that (estimated at 0.01% minimum) some residual peroxide is required. However, if the analysed amount of benzoyl peroxide, which is residual in the polymer, is instead added and dissolved in the proportionate amount of monomer and this mixed with the polymer from which the peroxide has been removed, the composition will become hard and unformable within several days. It is apparent from the foregoing that the monomer must have the characteristic of solvating the polymer but not extracting the peroxide until the curing step is to be carried out.

EXAMPLE I

VENEER GEL FORMULATION

90 grams of a suspension polymerized polymer of methyl methacrylate (clear beads 0.5-1.0 mm diameter), prepared by suspension polymerisation of methyl methacrylate with 10% by weight dibutyl phthalate and 0.5% by weight benzoyl peroxide, and having a residual content of about 0.1% by weight (specification requirement for teeth not more than 0.2%) benzoyl peroxide and molecular weight by viscosity of 500,000 was pigmented with:

F-2100 (fluorescent zinc oxide)	0.14 gr.
Permalba (titanium dioxide, magnesium sulphate)	0.025 gr.
Cadmium Yellow F-5512 (cadmium sulphide)	0.0015 gr.
Cadmium Red F-5893 (cadmium sulphide)	0.0010 gr.
Ivory Black (carbon black)	0.0005 gr.

The pigments were ball milled with 3 pounds of stones for 10 minutes before being mixed with 90 gr. of the methyl methacrylate polymer.

To 55 grams of pigmented polymer above were added 45 grams of SR-205 (triethylene glycol dimethacrylate) containing 200 p.p.m. hydroquinone. The mixture was stirred thoroughly and allowed to stand. At the end of 24 hours the viscosity was such that it would be considered "packable" by accepted dental techniques for crown and bridge acrylics. After seven days, the viscosity was ideal. Some slight increases in viscosity were noted in the next six months in which the gel was left in a jar at room temperature, but at the end of six months the gel could still be easily used for preparation of a veneer.

EXAMPLE II

A methyl methacrylate polymer was prepared using 0.2% azoisobutyronitrile as catalyst and the polymer was pigmented using different pigments as follows:

Methyl methacrylate polymer (Monsanto (RTM) B16)	90 gr.
F-2215 (fluorescent zinc oxide)	0.10 gr.
TiO_2 (titanium dioxide)	0.02 gr.
Cadmium Yellow F-6489 (cadmium sulphide)	0.0005 gr.
Cadmium Orange F-5895 (cadmium sulphide)	0.0008 gr.
Iron Black (iron oxide)	0.0002 gr.

This mixture was ball milled with 3 pounds of stones for 10 minutes.

To 70 grams of the above powder were added 30 grams of SR-210 (polyethylene glycol 200 dimethacrylate) to which were added 500 p.p.m. monomethyl ether of hydroquinone. The mixture was stirred. At the end of 8 hours a portion was removed and placed between polyethylene sheets in a slightly warmed mould (45°C.) and was pressed into a shape suitable for use as an incisor for an anterior tooth.

EXAMPLE III

To 60 grams of the methyl methacrylate polymer of Example II were added 40 grams of 1,6-hexamethylene glycol dimethacrylate to which 500 p.p.m. dimethyl cyclohexylamine were added. This mixture was stirred and allowed to stand for 7 days after which it was usable as a dough. The dough was processed to make an inlay as in Example VI.

EXAMPLE IV
TOOTH COMPOSITION

A bead polymer was prepared by a suspension polymerization of methyl methacrylate with 10% by weight dibutyl phthalate and 0.5% by weight benzoyl peroxide by the method of Example I. The molecular weight was 425,000. This polymer was pigmented as follows:—

Polymer	45.4 gr.
Brown concentrate * (burnt sienna)	0.366 gr.
Red concentrate * (cadmium selenide)	0.91 gr.
Yellow concentrate * (cadmium selenide)	1.530 gr.
Black concentrate * (carbon black)	3.660 gr.
TiO_2 (titanium dioxide)	1.3 gr.

*Made by using 1 part pigment and 99 parts polymer and ball milling.

The pigmented polymer was mixed in a muller for 5 minutes.

To 60 grams of the above polymer were added 40 grams of SR-205 (triethylene glycol dimethacrylate) containing 60 p.p.m. hydroquinone. The mixture was stirred and allowed to stand two days and made into a tooth as in Example VII.

EXAMPLE V

A polymer is prepared by a suspension polymerization of methyl methacrylate with 7% by weight dibtuyl phthalate and 0.4% by weight benzoyl peroxide. The molecular weight was 550,000. This polymer was pigmented as follows:

Polymer	45.4 gr.
Brown Concentrate * (burnt sienna)	0.366 gr.
Red concentrate * (cadmium selenide)	0.91 gr.
Yellow concentrate * (cadmium selenide)	1.530 gr.
Black concentrate * (carbon black)	3.660 gr.
TiO_2 (titanium dioxide)	1.3 gr.

*Made by using 1 part pigment and 99 parts polymer and ball milling.

The pigmented polymer was mixed in a muller for 5 minutes.

To 60 grams of the above polymer were added 40 grams of SR1205 (triethylene glycol dimethacrylate) containing 60 p.p.m. hydroquinone. The mixture was stirred and allowed to stand two days and made into a tooth as in Example VII.

EXAMPLE VI
CURING OF VENEER GEL AS AN INLAY

The normal procedure for preparing an inlay was followed. A body dough was prepared using Justi "Namilon" Shade "65"*. This body was cured in the flash for 15 minutes at 212°F. The top was then removed and the body material ground away to the desired shape of the incisal. The gel from Example I was placed on the surface of the body, and then the top of the slightly heated mould was pressed down. The gel tip was then cured at 212°F. for 30 minutes. The flask was cooled on the bench for 30 minutes, then the inlay broken out, finished, polished and finally inserted into a central tooth. There was no sign of wear, abrasion or colour change in this inlay for one year.

*Justi "Namilon" shade "65" is a pigmented acrylic polymer of grey-white hue of inorganic pigments as in Example V.

EXAMPLE VII
CURING OF THE TOOTH COMPOSITION

The tooth body composition as prepared in Example IV was formed as the surface of the body of posterior teeth and was formed around a core of lightly-cross-linked standard acrylic dough. This two layered body was cured in a metal mould such that the top of the mould was designed to follow

the desired contour of the body shape of the tooth. The material was cured for three minutes at 98°C. with 1700 p.s.i. The top of the mould was removed and an incisal disc made from the composition shown in Example IV was placed on the surface. A second top to the mould having the shape of the final tooth was placed on the surface and the mould placed in a press at 98°C. for 3 minutes. Finally, the mould was post cured for 3 minutes at 150°C.

The tooth prepared in this manner is hard and tough and withstood all the tests used for evaluating commercial and experimental teeth. It also grinds very hard (porcelain-like) on the wheel and can be polished to a high finish. The composition may, of course, only partly instead of wholly surround the core.

Shrinkage on polymerization of the triethylene glycol dimethacrylate (SR-205) is theoretically 69% of the comparative shrinkage of methyl methacrylate. Since the efficiency of polymerization is about 80%, the actual shrinkage is closer to 55% of methyl methacrylate. Thus, 55 parts polymer to 45 parts monomer of triethylene glycol dimethacrylate (SR-205) is very close to the 2 parts of copolymer to 1 part of methyl methacrylate monomer by weight when total shrinkage on polymerization is compared. In clinical tests this theoretical result is confirmed by the absence of "lakes" or "dents" which are observed in a crown when processed from a dough containing excessive monomer.

In each of the foregoing examples, the suspension polymer of methyl methacrylate was prepared by the standard procedure originally developed by Crawford and disclosed in U.S. Patent No. 2,108,044 and U.S. Patent No. 2,191,520, the preferred suspension stabilizing agents being either sarch or methyl cellulose. The particle size distribution is preferably between No. 80 Tyler sieve and No. 200 Tyler sieve when the polymer product in the formulations of the invention is employed for dental purposes. A typical distribution of the polymer powder which is useful for the dental applications of the invention is as follows:

TABLE I
PARTICLE SIZE OF POLYMER POWDER

Material	*Amount retained (%) by Tyler Sieve No.*					
	30	*60*	*80*	*100*	*200*	*Over 200*
Denture Base	0	1-5	30-40	20-30	10-15	1
Tooth Restorative	0	1-5	20-30	10-15	30-40	0.2-2

The powder particles intended for tooth restorative purposes are somewhat finer spherical granules than those for denture base structures. The tooth restorative products are otherwise similar to denture resins. Usually the powders are not uniform in particle size, but instead most products contain a controlled range of sizes.

The foregoing illustrative examples of particle size extend to methacrylate copolymers, the methacrylate copolymers being made by polymerizing liquid material containing, for example, 60% by weight methyl methacrylate and 40% by weight ethyl acrylate, or 30% by weight methyl methacrylate, 30% by weight butyl methacrylate and 40% by weight ethyl acrylate which have rubbery characteristics while retaining surface hardness, the products containing the higher proportions of methyl methacrylate being harder than the products containing the lower proportions.

As long as at least about 60% by weight of the liquid polymerizable monomer material is methacrylate ester, other polymerizable monomers may be added in limited amounts to modify the properties of the polymer, the resulting modification in properties being known in the prior art. Up to 40% by weight of vinyl aromatic monomers such as styrene, vinyl toluene, confer aromatic solvent-solubility to the product, and up to 40% by weight of acrylic acid esters of monohydric aliphatic alcohols having from 6 to 8 carbon atoms may be employed to provide an elasticizing action with improved adhesion to the solid polymer produced.

Up to 10% by weight of methacrylic acid, itaconic acid or acrylic acid may be mixed with the methacrylate ester.

Smaller particle size distribution may be provided by known methods of emulsion polymerization to achieve particle sizes between 0.01 and 0.4 micron.

Suitable catalysts for polymerization are the free radical polymerization catalysts such as peroxides, e.g. benzoyl peroxide, phthaloyl peroxide, acetyl peroxide, caproyl peroxide, lauroyl peroxide, cinnamoyl peroxide, acetyl benzoyl peroxide, methyl ethyl ketone peroxide, sodium peroxide, hydrogen peroxide, di-*tert*. butyl peroxide, tetralin peroxide, urea peroxide, the hydroperoxides, e.g., cumene hydroperoxide, *p*-menthane hydroperoxide, diisopropyl-benzene hydroperoxide, *tert*. butyl hydroperoxide, methyl ethyl ketone hydroperoxide, 1-hydroxycyclohexyl hydroperoxide - 1, azo compounds such as 2,2'-azo-bis-isobutyronitrile, 2,2'-azo-bis-isovaleronitrile, the per salts, e.g. ammonium persulphate, sodium perborate, sodium perchlorate, potassium persulphate.

The catalysts may be used alone or in

admixture with one another. Benzoyl peroxide is the preferred catalyst. Any suitable amount of the catalyst sufficient to polymerise the composition may be used, but in general the catalyst concentration that gives satisfactory results may be within the range of 0.1 and 2.0 per cent by weight of the entire polymerizable mass. Curing of the polymerisable composition is preferably effected at a temperature of 212°F for longer than fifteen minutes.

In dental compositions, use may also be made of vermilion, sulphides of mercury, and cadmium red with zinc or titanium oxide to produce the desired pink shade in denture base resin. Cadmium yellow can be used for deep yellow to orange colour. Such pigments as carbon black and the oxides of iron, zinc or titanium are harmless and may be employed with success to produce various shades of grey and brown. The burnt and raw umbers and siennas, and the ocres are useful for producing variations in brown shades. Other useful pigments for specific shadings include ultramarine blue and chrome green and yellow. The pigments employed in dental porcelain can be utilised also for methacrylate crown and inlays, while any pigment employed in dental rubber can be used in the mixture of the invention. Soluble dyes often tend to bleach to a lighter shade in the mouth, for which reason they are generally undesirable. In the commercial dental products now available, the pigments are usually all fairly stable. Except for the clear transparent shades, most resins have varying degrees of opacity. The oxides or zinc or titanium serve as opacifying agents. Titanium dioxide is the more effective of the two, so that only minute quantities are required.

Various effects can be produced. Thus, the composition may advantageously be relatively heavily pigmented at an inner layer thereof to provide the body shade and less heavily pigmented at the occlusal tip portion. Alternatively, the extremity of said tip portion may be non-pigmented, portions immediately adjacent said extremity being gradually darker in pigmentation to provide intermediate shading between the transparent tip and the body portion.

CURING OF CROWN AND BRIDGE AND VENEER GEL.

The preferred method utilized 30 minutes in a plaster or stone mould in a water bath at 212°F.

It is also possible to heat the gel with a hot lamp press and form it with a mould, remove the mould, and complete the cure with the hot lamp. This cure generally takes 15 minutes or less. One disadvantage of not keeping on the mould top is the inability to retain exact detail of the mould. However, for many uses this is unimportant. The tooth may be shaped additionally by curing during pressing with a hot tool.

The preferred method for moulding the present composite tooth is by compression moulding at a relatively low temperature in a metal mould or dental flask, e.g., about 217°F. and utilizing high pressures of 2000-10000 psi to achieve maximum density flask and gloss porcelain-like surface. Tooth products so made are characterized by dimensional tolerances as close as 0.0005 inch.

The following are suitable liquid difunctional dimethacrylate and diacrylate esters for the composition for manufacturing moulded teeth:

Diethylene glycol dimethacrylate
Triethylene glycol dimethacrylate
Tetraethylene glycol dimethacrylate
Polyethylene glycol 200 dimethacrylate
Polyethylene glycol 400 dimethacrylate
Polyethylene glycol 600 dimethacrylate
Neopentyl glycol dimethacrylate
Tetramethylene glycol dimethacrylate
Hexamethylene glycol dimethacrylate
1,3-Butylene glycol dimethacrylate
1,3-Propylene glycol dimethacrylate
Diethylene glycol diacrylate
Triethylene glycol diacrylate
Tetraethylene glycol diacrylate
Polyethylene glycol 200 diacrylate
Polyethylene glycol 400 diacrylate
Polyethylene glycol 600 diacrylate
Neopentyl glycol diacrylate
Hexamethylene glycol diacrylate
1,3-Butylene glycol diacrylate
1,3-Propylene glycol diacrylate

For medium temperature curing, e.g., 60-100°C., benzoyl peroxide or lauroyl peroxide may be used. Azobisisobutyronitrile is a typical example of an azo free radical catalyst which gives a high degree of polymerization product at lower temperature, e.g., 60°C., and a lower degree of polymerization product at higher temperature, e.g., 75-100°C.

Promoters, such as aromatic amines, ascorbic acid, cobalt salts or REDOX activators, may be used with the free radical polymerization catalyst, such as organic or inorganic peroxide.

The tertiary amine activators are particularly preferred, such as N,N-dimethylaniline, N,N - dimethyl-p - toluidine, N,N - dimethylcyclohexyl amine, or trihexylamine with such syrups. This type of activator is used with advantage in the denture applications of the invention.

The use of peroxides in the polymerization process does not require careful control of polymerization, particularly during the accelerated exotherm stage as in the curing of polyesters, in order to obtain a bubble-

free product with good clarity. The present mixtures may be polymerized using more than one catalyst over more than one temperature. The present mixture may be used in essentially the same manner, as in the use of methacrylate for embedding purposes.

The great advantage may be had by using peroxide catalyzed bulk polymerization of methyl methacrylate to form the solid polymer, since after 20-30% conversion to polymer, the rate of polymerization is greatly accelerated, and this rate of acceleration is accompanied by a corresponding increase in the degree of polymerization.

Glass-filled doughs may be used in the fabrication of reinforced parts where moulding difficulties are encountered with standard methods.

Preferably, chopped glass fibres in conjunction with supplementary fillers are used, the fibre content varying from 5 to 30% by weight, depending on the ratio of the supplementary fillers. The filled putties may be performed. The moulded part provides smooth surfaces with few flow lines at the areas of glass orientation and any temperature of curing may be used as desired.

The preformed putty in strip form is protected in a package form by supporting it on a detachable facing sheet or by containing it between detachable facing sheets. The preformed putty strip can be cut into slugs. In this form, it is useful for patching and restoring by polymerizing it at elevated temperatures of about 212°F. or above, and at elevated pressures, if desired.

The putty in strip form may be used as a veneer forming an outer dental facing for a core of methyl methacrylate polymer, moulded and cured to form a tooth.

An exposed portion of the tooth will contain the solid, finely divided, methyl methacrylate polymer in the outer portion which is plasticized with a non-volatile ester plasticizer, such as dibutyl phthalate, whereby the uniform dispersion of the polymer is enhanced.

WHAT WE CLAIM IS:—

1. A pasty, polymerizable, synthetic resin dough composition consisting of a polymerizable mixture of a solid, finely divided methyl methacrylate polymer and a polymerizable, liquid dimethacrylate or diacrylate ester, said ester being the sole liquid component of the composition and being derived from a polyhydric aliphatic alcohol containing from 3 to 8 carbon atoms, or a polyethylene glycol having a degree of polymerization from 2 to 6 or a polypropylene glycol having a degree of polymerization from 2 to 6, said ester being less volatile than dibutyl phthalate.

2. A composition according to claim 1 in which said alcohol is an aliphatic glycol.

3. A composition according to claim 1 or 2 in which said alcohol contains from 5 to 8 carbon atoms.

4. A composition according to claim 3 in which said ester is triethylene glycol dimethacrylate.

5. A composition according to claim 3 in which said ester is tetraethylene glycol dimethacrylate.

6. A composition according to claim 3 in which said ester is 1, 3 butylene glycol dimethacrylate.

7. A composition according to any preceding claim including an opacifying, inert, stable, solid pigment.

8. A composition according to claim 7 in which said pigment is titanium dioxide, zinc oxide, copper oxide, iron oxide, cobalt oxide, barium sulphate, carbon black, burnt umber, cadmium selenide, or cadmium sulphide, or mixtures thereof.

9. A composition according to any preceding claim in which said polymer is prepared by peroxide polymerization and contains an amount of peroxide sufficient to polymerize said composition when the latter is heated to a curing temperature of 212°F for longer than fifteen minutes.

10. A pasty, polymerizable, synthetic resin dough composition according to claim 1 substantially as hereinbefore described.

11. A dental package comprising a supporting sheet and a preformed strip of a composition according to any preceding claim which is readily detachable from said supporting sheet.

12. A dental package according to claim 11 wherein said strip is contained between top and bottom detachable sheets.

13. A dental package incorporating a composition according to claim 1 substantially as hereinbefore described.

14. A composite artificial tooth including an inner core portion of solid polymethyl methacrylate, and a polymerised or cured polymerisable composition according to any one of claims 1 to 10 applied so as to wholly or partly surround said inner core to form an outer exposed portion of the tooth.

15. A composite artificial tooth according to claim 14 in which said composition is pigmented relatively heavily at an inner layer thereof to provide the body shade and is less heavily pigmented at the occlusal tip portion.

16. A composite artificial tooth according to claim 15 in which the extremity of said tip portion is non-pigmented and portions immediately adjacent said extremity are gradually darker in pigmentation to provide intermediate shading between the transparent tip and the body portion.

17. A composite artificial tooth according to any one of claims 14 to 16 in which said exposed portion contains said solid,

finely divided, methyl methacrylate polymer in the outer portion which is plasticized with a non-volatile ester plasticizer, whereby the uniform dispersion of said polymer in said liquid is enhanced.

18. A composite artificial tooth according to claim 17 in which said plasticizer is dibutyl phthalate.

19. A composite artificial tooth incorporating a polymerised or cured polymerisable composition according to claim 1 substantially as hereinbefore described.

20. An inlay for an artificial tooth comprisng a polymerised or cured polymerisable composition according to any one of claims 1 to 10.

21. A veneer for an artificial tooth comprising a polymerised or cured polymerisable composition according to any one of claims 1 to 10.

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